

# Energy of bond defects in quantum spin chains obtained from local approximations and from exact diagonalization

V. L. Líbero<sup>\*</sup>, K. Capelle, F. C. Souza, A. P. Fávaro

*Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil*

## Abstract

We study the influence of ferromagnetic and antiferromagnetic bond defects on the ground-state energy of antiferromagnetic spin chains. In the absence of translational invariance, the energy spectrum of the full Hamiltonian is obtained numerically, by an iterative modification of the power algorithm. In parallel, approximate analytical energies are obtained from a local-bond approximation, proposed here. This approximation results in significant improvement upon the mean-field approximation, at negligible extra computational effort.

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## 1. Introduction

Many different types of magnetic systems are commonly modeled by spin Hamiltonians, such as the Heisenberg model. In special limits, such model Hamiltonians can be solved analytically, e.g., by the Bethe Ansatz for integrable one-dimensional systems. Away from special limits, powerful numerical methods, such as Monte Carlo simulations or density-matrix renormalization group techniques, provide much useful information, but at high computational cost. Full exact diagonalization is even more expensive, and thus limited to rather small systems. Quite generally, analytical and numerical techniques work best for models in which all sites are equivalent, so that translational invariance can be used to reduce the complexity of the problem.

In magnetic nanostructures[1] and molecular magnets[2], the generic many-body features of spin Hamiltonians coexist with additional real-life complications, such as impurities, defects, boundaries, textures, etc. The resulting *spatially inhomogeneous* spin Hamiltonians do not have translational symmetry, and often also lack other simplifying symmetries, which makes them hard to treat by traditional analytical and numerical methods.

Mean-field theory can, of course, always be applied, but is not sufficiently reliable to permit quantitative modeling, and is often even qualitatively wrong. In this paper we de-

scribe one analytical and one numerical method to obtain beyond-mean-field energies for spin chains without translational invariance.

The analytical calculations are based on model density-functional theory (DFT). In *ab initio* electronic-structure calculations DFT[3] is a useful way to include correlations beyond the mean-field approximations, at very little additional computational cost. To deal with defects within DFT for spin chains, we propose a local-bond approximation (LBA), akin to the local-density approximation (LDA) of *ab initio* DFT and the local-spin approximation (LSA) previously proposed for spin systems with impurities[4,5,6,7]. These schemes are described in Sec. 2.

To obtain results with higher precision than is possible by local approximations, and to judge the performance of such simple improvements on mean-field theory, we also perform fully numerical calculations, employing an iterative modification of the power algorithm, described in Section 3. Representative results are discussed in Section 4.

## 2. Local approximations for spin Hamiltonians

DFT has been applied to model Hamiltonians, such as the Heisenberg[4,5,6,7] and the Hubbard[8] model, within generalized local-density approximations. Specifically for the Heisenberg model with impurity spins, this scheme consists in adding to the mean-field energy a local approximation to the correlation energy  $E_c$ , of the form

<sup>\*</sup> Corresponding author. Tel+55-16-33739854; fax+55-16-33739877  
Email address: [libero@if.sc.usp.br](mailto:libero@if.sc.usp.br) (V. L. Líbero).

$$E_c^{LSA}[J, S_i] = \sum_i e_c^{hom}(J, S) |_{S \rightarrow S_i} \quad (1)$$

where the sum runs over all sites  $i$ , and  $e_c^{hom}(J, S)$  is the per-site correlation energy of the homogeneous spin  $S$  Heisenberg model, for which various approximations exist[4,5]. This so-called local-spin approximation[4,5] has been applied to investigate the energetics of impurities in one, two and three-dimensional Heisenberg models[4,5,6,7]. Impurities here are defined, relative to a homogeneous model in which all sites have the same spin  $S$ , as sites with a spin  $S_I \neq S$  (see inset of Fig. 1 for an example).

Another important class of spatial inhomogeneity, defects, cannot be treated within the LSA. We define defects, again with respect to a homogeneous model, as bonds having strength  $J_D \neq J$  (see insets of Figs. 1 and 2 for examples). To extend the local-approximation scheme to spin Hamiltonians with defects, we here propose the *local-bond approximation (LBA)*,

$$E_c^{LBA}[J_b, S] = \sum_b e_c^{hom}(J, S) |_{J \rightarrow J_b}, \quad (2)$$

where the sum runs over all bonds  $b$ , and for  $e_c^{hom}(J, S)$  we use the same expressions employed in the LSA. Conceptually, the LBA decomposes the system in bonds, acting between sites, whereas the LSA decomposes it in sites, connected by bonds. Both approximation schemes become exact for infinite homogeneous systems, and both can be used in analytical calculations, as all one has to do to obtain corrections to the mean-field energies is to evaluate Eqs. (1) or (2) site by site or bond by bond.

### 3. Numerical Ground-State Energy

To obtain energies of higher quality than is possible with analytical calculations employing local approximations, we resort to a numerical scheme. Even in the presence of impurity spins and/or bond defects, the Heisenberg Hamiltonian

$$\hat{H} = \sum_i J_i \hat{S}_i \cdot \hat{S}_{i+1}, \quad (3)$$

where  $J_i$  is the exchange integral between nearest-neighbor spin-vectors  $\hat{S}_i$  and  $\hat{S}_{i+1}$ , conserves the  $z$ -component of the total spin,  $\hat{S}_z$ . The Lieb-Mattis theorem guaranties that the GS pertains to the subspace of minimum  $|S_z|$ . As basis vectors we therefore use the set of quantum numbers  $\{|m_1, m_2, \dots, m_N|\}$ , where  $m_i$  are the eigenvalues of  $\hat{S}_i$ , and can take values  $-S_i, -S_i + 1, \dots, S_i$ . A practical way of generating this set of states is by decomposing integer numbers. For instance, for a chain with four spins  $1/2$ , the binary decomposition of the integer 6 gives the sequence 0110, representing the vector  $|-1/2, 1/2, 1/2, -1/2\rangle$ , one among other five of the subspace with  $S_z = 0$ . It is straightforward to assemble the matrix representation of  $\hat{H}$  in this base. However, although the resulting matrix is sparse, storing it is impractical: for 20 spins  $1/2$  the order of the matrix is 184756, with 1108536 non-vanishing elements. In practice,

we therefore do not store the matrix, but compute each matrix element every time it is needed; this saves a lot of memory, but is time consuming.

To obtain the ground-state energy of  $\hat{H}$  we propose an iterative modification of the well-known power algorithm. This modification, to be described in more detail in a separate publication, is easy to code and requires less memory than the Lanczos method, although it typically takes more processing time to extract the ground state. The power algorithm starts by decomposing a trial function for the ground-state eigenvector in terms of the unknown eigenvectors  $|\psi_n\rangle$  of  $\hat{H}$ , according to  $|\psi_T\rangle = \sum_n \alpha_n |\psi_n\rangle$ , with  $\alpha_n$  constants. If  $\epsilon$  is an upper limit of the energy spectrum, acting  $k$  times with the operator  $\hat{H} - \epsilon$  on  $|\psi_T\rangle$  yields

$$(\hat{H} - \epsilon)^k |\psi_T\rangle = \sum_n \alpha_n (E_n - \epsilon)^k |\psi_n\rangle, \quad (4)$$

where  $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ . For antiferromagnetic chains, the highest energy  $\epsilon$  corresponds to the ferromagnetic configuration, whose value is trivial even in the presence of impurities or defects. For  $k \rightarrow \infty$ , the above series is dominated by the ground-state term  $\alpha_0 (E_0 - \epsilon)^k |\psi_0\rangle$ . Therefore, we can extract  $E_0$  by performing

$$E_0 = \lim_{k \rightarrow \infty} \frac{\langle \phi | (\hat{H} - \epsilon)^{k+1} | \psi_T \rangle}{\langle \phi | (\hat{H} - \epsilon)^k | \psi_T \rangle} + \epsilon, \quad (5)$$

where  $|\phi\rangle$  is any vector non-orthogonal to the ground state. Without the constant  $\epsilon$ , the method yields the highest (in modulus) eigenvalue instead. Our experience shows that the best trial function is the Néel state, a mean-field approximation for the ground state, consisting of a sequence of an up and down spins.

To speed up the search for  $E_0$ , we implement the above limit iteratively: at each step  $k$ , we use for  $|\phi\rangle$  the state  $|\phi_{k-1}\rangle = (\hat{H} - \epsilon)^{k-1} |\psi_T\rangle$  obtained in the previous step. This reduces the processing time to reach convergence, which we characterize by two successive values of  $E_0/N$  differing by less than  $10^{-13}$ . Typically, a few hundred  $k$ -steps are required for chains larger than 20 spins, and only a few dozens for smaller chains. Using a desktop microcomputer with 1.5 MB of RAM, we obtained the ground-state energy of a homogeneous chain with 30 spins  $1/2$ , reproducing the results of Ref.[9]. Bond defects do not require more memory space.

### 4. Antiferromagnetic spin chains with ferro- and antiferromagnetic defects

As a first application of the LBA concept we compare, in Fig. 1, an antiferromagnetic (AFM) spin  $1/2$  ring (periodic boundary conditions) with one impurity spin  $S_I = 3/2$  to an AFM spin  $1/2$  ring with one bond defect  $J_D = 5J$ . In the mean-field approximation, both systems are, erroneously, predicted to have the same ground-state energy. This spurious degeneracy is lifted by adding the LSA and LBA correlation energies, respectively. Judged by the re-

maintaining distance to the exact data, LSA performs slightly better for the impurity than LBA does for the defect, but both provide significant improvements on the mean-field data.

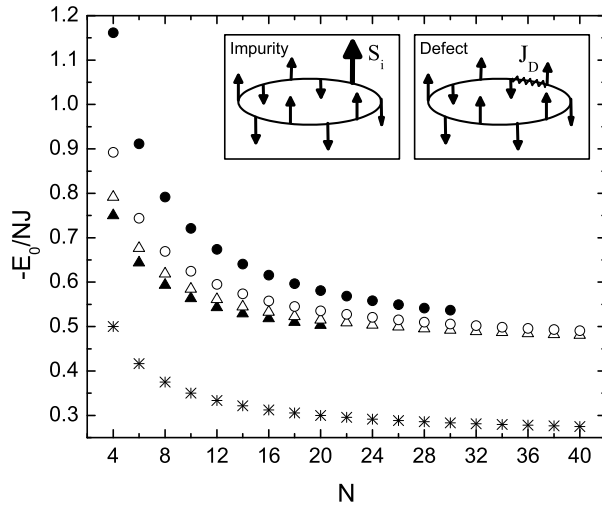


Fig. 1. Ground-state energy of an AFM spin 1/2 ring with a spin 3/2 impurity (triangles), and with an AFM defect of strength  $J_D = 5J$  (circles), treated exactly (filled symbols) and via local approximations LSA/LBA (open symbols). Within mean-field theory (stars), the impurity and the defect yield the same ground-state energy. Inclusion of correlation energy in the LSA (impurity case, open triangles) and the LBA (defect case, open circles) removes this spurious degeneracy.

Ferromagnetic (FM) defects, with  $J_D < 0$ , can be handled similarly. However, an ambiguity arises in how the local substitution is to be performed. In principle, the LBA can be applied to a FM defect by substituting  $J \rightarrow |J_i|$ ,  $J \rightarrow J_i$  or  $J \rightarrow \delta_{J_i, |J_i|}$ . The first possibility can lead to positive correlation energies, in violation of the variational principle. The second and third possibilities correctly predict negative correlation energies, but numerically the second is slightly inferior to the third for the type of system investigated here, as judged by comparison to exact data. Below, we thus employ the third substitution. Physically, this choice,  $J \rightarrow \delta_{J_i, |J_i|}$ , means that a ferromagnetic bond does not contribute to the correlation energy, which is rather reasonable, as at zero temperature the mean-field energy of a homogeneous ferromagnetic chain is already exact.

In Fig. 2 we show ground-state energies of an AFM spin chain (open boundary conditions) with one AFM defect  $J_D = +3J$ , and of the same chain with one relaxed FM defect,  $J_D = -3J$ . Comparison of LBA data with exact data shows that the LBA significantly improves on the mean-field approximation both for FM and AFM defects. Quantitatively, the performance for the FM defect (squares in Fig. 2) is better than that for the AFM defect, but in both cases a significant improvement over the mean-field data is achieved. Note, in particular, that for an FM defect the mean-field curve is even qualitatively wrong, predicting a wrong sign for the slope at  $N \rightarrow 0$ , whereas the LBA recovers the correct behavior.

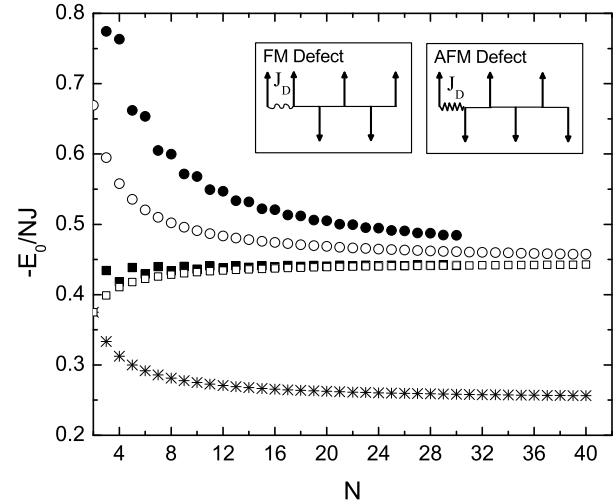


Fig. 2. Ground-state energy of an AFM spin 1/2 chain with an AFM defect of strength  $J_D = +3J$  (circles), and with an FM defect of strength  $J_D = -3J$  (squares). Exact data (full symbols) are compared to LBA data (open symbols) and mean-field data (stars).

We stress that the LBA calculations for both AFM and FM defects, as well as LSA calculations for impurities, can be done analytically, in any dimensionality and for any system size, regardless of boundary conditions and symmetries. Such local approximations thus provide a very convenient way to obtain beyond-mean-field results at the expense of a conventional mean-field calculation. When used in this way, local approximations yield robust results of moderate precision, even for large and complex systems.

High precision results, on the other hand, cannot be expected from simple local approximations. Improved algorithms for fully numerical diagonalization, such as that described in Section 3, can be used to make progress from exactly the opposite starting point: high precision for small systems.

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